THE

COMMERCIAL ANALYSIS

OF

FURNACE GASES.

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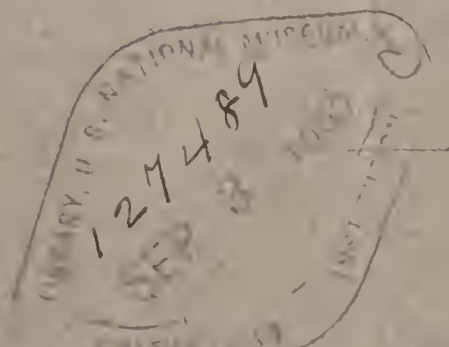
THE COMMERCIAL ANALYSIS OF FURNACE GASES.

THE importance of making analyses of gases in furnaces which are used for metallurgical purposes is every day growing more and more evident. It is the only method of understanding the reactions that take place in the furnace, and of economically conducting the operations both with regard to the fuel used and the reactions which take place on the bodies to be subjected to the influence of the heat and gases.

As a knowledge of the composition of gases is becoming every day more necessary to the proper conduct of furnace operations, it seems desirable that furnace managers should generally know that the analysis of gas for commercial purposes is neither difficult, tedious, or expensive, and that it does not necessarily imply the use of corrections requiring difficult instrumental observations and long and tedious mathematical calculations.

Any method, therefore, which will tend to render these analyses simple will also tend to having them made and repeated as frequently as the analyses of the ores and other materials charged in the furnace. They should be made even more frequently, as their composition is affected by any change in the condition of the furnace, and a knowledge of their composition will give a ready clue to the unseen and otherwise not easily detected changes which are taking place.

The only practicable method of making industrial analyses of gas is that of measuring volumes in graduated tubes. The methods by direct weight are too long and too complicated for commercial uses. The method by volumes has the double advantage that it can be made so exact in the hands of an expert as to be suitable for ultimate analyses, or it may be made so simple as to be within the capabili-

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ties of a common workman, who may be easily taught to determine volumes to within one-half per cent., which is a sufficiently close approximation for any industrial purpose.

It may be said in general terms that the normal working of any furnace will depend upon the ratio of $\frac{CO_2}{CO}$, and that it is in keeping the ratio of these two gases in proper relations that successful management depends. For ordinary commercial operations this relation can be determined in a few minutes, and is all the more important since it is desirable to know what it is, both at the entry of the gas into the furnace, and at its exit either into flues or into the air. By determining what this normal relation should be, it is quite possible to foresee the working of blast furnaces twenty-four hours ahead, and thus provide against accidents, and sometimes to bring down the consumption of fuel, and extend the length of a campaign very greatly. Accidents in blast furnaces will generally show themselves in their first stages in the composition of the gas at least twenty-four hours before they manifest themselves at the tuyeres or in the slag. An examination of the gas will, therefore, give a ready means of preventing them.

It is not usually sufficient for this, however, to make single analyses at intervals; it is necessary that they should be repeatedly made, and that, as a general rule, the taking of the sample of the gas should be continued over several hours.

While in some industrial gases the hydrocarbons, sulphurous acid, and occasionally chlorine are to be determined, for ordinary metallurgical purposes, the determination of carbonic acid, carbonic oxide, oxygen, and nitrogen (which will be the residue), only is necessary, since these are the gases which are principally affected by the process. As a general thing the hydrocarbons, except in generators, are not found in any considerable quantity; nor is oxygen, except in furnaces where its presence is certain beforehand on account of its introduction in large quantities with air. To perform such an analysis in the works for commercial purposes the modified Orsat apparatus is the one which it is advisable to use.

Since the description of the Orsat apparatus was published in Vol. II of the *Transactions of the Institute,* a large number of furnace managers have introduced it into their works, and are daily making use of it to control the working of their furnaces. The constant demand made for it in Europe and in this country has led to important modifications; and the importance of having a simple apparatus which can be put into the hands of workmen has brought about

several changes which tend to make it more portable and more complete.

The Orsat apparatus as now modified does not differ in principle from that described in Vol. II of the *Transactions*. There has been added to it an appendage for the determination of hydrocarbons, which makes the apparatus more complete and useful in cases where mine gases are to be analyzed for the detection of fire-damp or for the examination of producer gases or any other gas. The shape of the apparatus, however, is somewhat different, the jars and bell glasses being replaced by U tubes. The volume of absorbent liquid used is also smaller, and the apparatus can consequently not be used so long without changing the liquid. This is, however, not a practical difficulty, as the number of analyses, as was shown in *Transactions*, Vol. II, page 234, can be almost indefinite.

This apparatus as now modified is shown in Fig. 1. It consists of a measuring-tube, A B, which is surrounded by water in order to have the gas at a constant temperature, and thus avoid the necessity of thermometers. The measuring-tube is open at both ends, and is fitted into the cooling tube by means of india-rubber corks. The bottom of the measurer is connected by means of a rubber tube with a small bottle, D, having an opening at the bottom, which contains acidulated water, and which is to serve both as an aspirator and expulsor of gas. The other end is connected with a small tube, which is not over a millimeter in diameter, which goes to the left of the measuring-tube. It has four arms, G, G′, G″, and I, each of which is provided with a glass stopcock. The prolongation of the tube itself is also provided with one at *C*. The one at the end connects with a tube, P, which is filled with cotton in order to filter smoke or dust from the gas which is drawn into the instrument through the rubber pipe, *N*. This filter connects by a glass tube at right angles, having a stopcock, R, with a trompe, L M, which is used both for aspiration and for clearing the apparatus of gas by connecting it with a water-bottle by the tube, K.

Each one of the U tubes is fitted to a wooden upright to which it is raised. The whole is then secured to the frame by thumbscrews, so that it can be easily removed to refill the tubes or alter the solutions.

A German modification of the apparatus has the tubes with the stopcocks made of pewter. This is a very objectionable form of it, as it is much more likely to become foul.

In order to be sure that the samples of gas taken for analyses

represent the mean composition of the gases, they should be taken through a pipe with a long slot, and the gas collected should be passed through a Liebig condenser before it is used, so that it may be quite cool before it is introduced into the apparatus. The three stopcocks nearest the measurer connect with the U tubes, the first

FIG. 1.
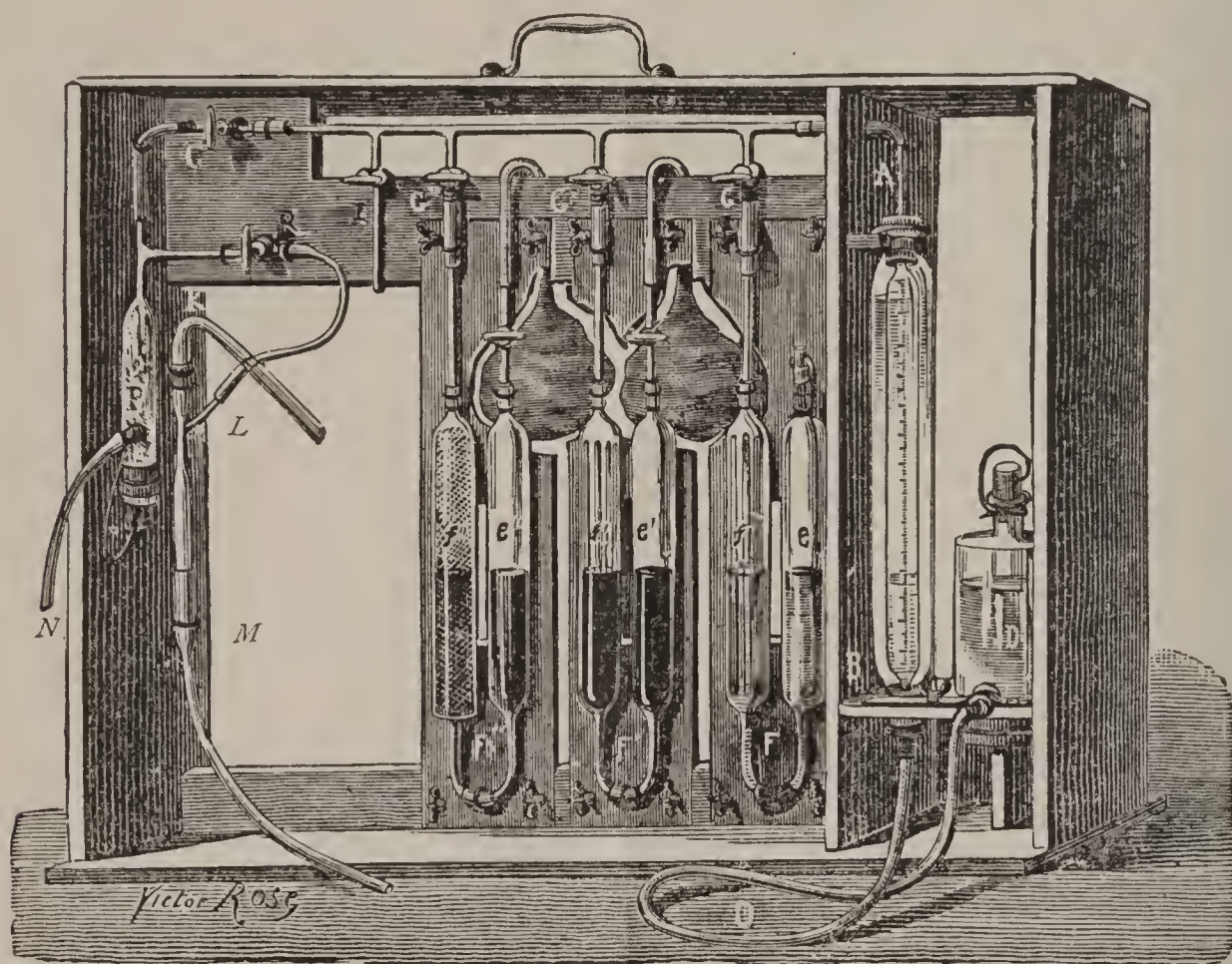
one of which, $e\,f$, contains potash; the second, $e'\,f'$, pyrogallate of potash; and the third, $e''\,f''$, an ammoniacal solution of chloride of copper. The first is destined for the absorption of carbonic acid, the second for the absorption of oxygen, and the third for the carbonic oxide. These last gases may be determined together as described in Vol. II. When only the gases of a blast furnace are to be analyzed, two tubes are all that are necessary, but as the extra tube does not increase the difficulty of manipulation and the extra cost is very slight, it is generally best to have three, as then the apparatus can be used in many cases where it would not be convenient to use two.

A considerable difficulty has been found in the use of the ammoniacal solution, it having been found to absorb very slowly. This solution, in order to have the greater surface, is formed by placing a roll of copper-wire gauze in the tubes. In order to get the requisite amount of surface it has been found desirable, with some gases, to replace this copper-wire by copper disks with short pieces of glass

tubing between them. The slowness with which this solution works is caused, however, by the fact that the salt which produces the absorption is not always present. The ammoniacal solution of chloride of copper absorbs oxygen very rapidly and forms an oxychloride of copper. When the oxychloride is formed the solution is blue, and when it is in this condition it absorbs the carbonic oxide rapidly ; but after a number of passages, the solution works very slowly and becomes green. In this case the oxychloride of copper, which is the absorbent, has been entirely used up, and it is necessary to make the solution blue again by the absorption of oxygen from the air, when it will absorb again as rapidly as at first.

As the pyrogallate and oxychloride solutions are very sensitive, the ends of the U tubes, e' f' and e'' f'', instead of being freely opened to the air are connected with rubber bags, the object of which is to prevent the access of the atmosphere. The oxygen of the air contained in the bags becomes rapidly absorbed, and the gas between the top of the solution and the interior of the bag in a short time will be composed of nothing but nitrogen. The details for using the left side of the apparatus are fully described in the article in Vol. II. In the complete apparatus, Fig. 2, the gallery is continued to the right, having a stopcock, J, on the gallery itself, and one projecting tube, E, with a stopcock. The end of the gallery is attached to a spiral platinum tube, T (which is to be heated by an alcohol lamp, or by a Bunsen gas-burner placed below it), which connects with a stopcock, V, below it, by which the supply of gas is regulated. The apparatus is arranged for one or the other or both means of heating the platinum tube. There are connected with this gallery two U tubes, one of which, g' h', serves as a reservoir, and the other, g h, is used for the production of hydrogen, which, with a large excess of air, is used to burn the hydrocarbons. There will be no danger, however, of an explosion, on account of the great excess of nitrogen and the capillarity of the tube. To insure complete combustion, the gas is mixed with a mixture of hydrogen and air.

The gas having been passed through the left side of the apparatus, is transferred from the measurer to the capillary tube, and from there into the U tube, g' h' (partially filled with water), which serves as a reservoir for the gas. The other U tube, g h, which serves for the production of hydrogen, is cut off from the gallery by a stopcock, E, while the transfer is made. It contains zinc and sulphuric acid, which, formed under pressure, throws the liquid back into the opposite side, thus forming a reservoir of hydrogen, and preventing

the attack of the zinc except when it is necessary. In order to prevent the waste of zinc while the apparatus is not in use, the acid is cut off by the stopcock, X, which also serves to empty both tubes when it is necessary.

FIG. 2.

When the hydrocarbons are to be determined, 200 divisions of the gas are taken, and all the gases that can be determined on the left side are separated first; 40 to 50 divisions are then taken for analysis, and all the remainder of the gas turned into the pyrogallate

solution, f' e'. Ten to fifteen divisions of hydrogen, and 130 to 150 of ordinary air, taken through the tube, N, are then introduced, the quantities being determined by the supposed amount of hydrocarbons present. The lamp, U, is lighted, and the mixture made to pass very slowly three or four times back and forth through the platinum spiral, T. Great care must be used not to introduce moisture into the platinum tube for fear of an explosion, which would break the glass tubes. The gas is then passed into the measurer, A B, and cooled, and the contraction read. In the burned gas carbonic acid and oxygen are determined. If there is no oxygen the combustion has not been complete, as there has not been sufficient air, and fresh air and hydrogen may be added, or, better, the analysis may be commenced over again by using the reserve in the pyrogallate tube. Complete combustion thus transforms the carbon into carbonic acid, and the hydrogen into water.

The carbonic acid is determined directly by its absorption in the potash tube, e f. The amount of water produced must be calculated; this is very easily done, for the quantity of air introduced is known, and if the number of divisions of it is represented by m, we have .021 m of oxygen, and .079 m of nitrogen; the nitrogen is unaffected and remains behind, while the .021 m of oxygen has been used to burn the hydrogen introduced into the U tube, and both the hydrogen and carbon of the hydrocarbon. Some of it has not been used, as the air must be in excess in order to be sure that the combustion has been complete.

Of these four quantities, three are known. Oxygen in excess has been determined in the pyrogallate solution. The quantity of hydrogen introduced is known. It has required for its combustion one-half its volume of oxygen. The carbon of the hydrocarbons has been transformed into carbonic oxide, to do which has required a volume of oxygen equal to its own. These volumes all being known, the quantity of oxygen used to burn the hydrogen of the hydrocarbons is consequently known by difference. This quantity of oxygen has produced double its volume of water, and, consequently, all the elements for making the calculation of the hydrocarbons are known.

The total volume of the hydrocarbons can also be determined, for after all the determinations have been made, the measuring-tube contains only nitrogen. This nitrogen is the sum of that contained in the gas and of that introduced with the air used to burn the carbon and hydrogen. The nitrogen contained in the gas was determined

before the gas passed the platinum spiral.   The nitrogen in the air is known from the quantity of air introduced.   Hence all the elements are determined.

This method is sufficiently exact for all commercial purposes; the only inconvenience that it has is from the fact that as the oxygen to burn the carbon and hydrogen is all derived from the air, a quantity equal to fifteen times the total amount of the hydrocarbons to be analyzed must be introduced, besides which another amount must also be added sufficient to burn the hydrogen.   This method is for commercial purposes much preferable, however, to using oxygen, as pure oxygen cannot always be had, and it would generally be impracticable to have it on hand for industrial operations; besides which, the method is only a commercial one.   Its errors, however, may be made to be not over one-half per cent. These errors are caused by the fact that the hydrocarbons are slightly soluble in the copper solution, and that acetylene, which some of these gases contain, precipitates the copper as an acetylide of copper.   It is therefore not well adapted to complete analyses of hydrocarbons, or for the analysis of illuminating gas, but sufficiently exact to determine the presence of hydrogen and hydrocarbons in furnace gases or in fire-damp in mines, or for any ordinary commercial purpose.   The very slight error is not sufficient to make any material change in determining the caloric powers of the different substances examined.